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Thermal and Oxidative Decomposition of Lower Fatty Acid with Special Attention to Formic Acid

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Abstract. Low molecular carboxyl acids are important intermediate products of wet combustion of organic pollutants. This article deals with the reaction rates and mecanisms of some of these acids under wet oxidation conditions. It appears from the investigations that the rate of decomposition increases by the number of carbon atoms as larger molecules decompose into smaller ones and CO_2. An exception is formic acid, the lower end member of the fatty acid series, which decomposes by both oxidative and non- oxidative routes at a rate several times higher than that of the other compounds tried.

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Contents

Introduction

The recent years have seen a growing interest in wet oxidation as a method for decomposing organic pollutants. The main reaction products are CO_2 and H_2O, but lower fatty acids are important intermediates. This report deals with the reaction rates and ways of decomposition of some of these acids under wet oxidation conditions.

1. Thermal Decomposition of Dilute Aqueous Formic Acid Solutions

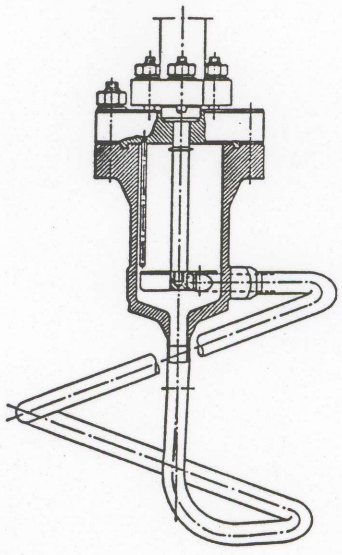
Among the refractory compounds formic acid is sometimes mentioned on equal terms with acetic acid (1,2). This contradicts what is stated elsewhere about the stability of formic acid (3,4,5). The last-mentioned results relate, however, to experiments with gaseous reactants. We have therefore found it worthwhile to carry out experiments to elucidate the decomposition of dilute aqueous solutions of formic acid under varying conditions.

1.1. Materials and Methods

Formic acid 98-100%, acetic acid 96% and sodium formiate, all Merck analytical grade, were dissolved in deionized water. The pertinent gas phase O_2 or N_2 was supplied from ordinary cylinders.

The apparatus used was a loop-autoclave described previously (6), which is characterized by a short heating and cooling period. For sampling, the autoclave must be opened after concluding the experiments. Two specimens of this autoclave have been manufactured from different materials. One (A) was made of Uddeholm acid-resistant steel UHB 24 (17.2% Cr, 11.1% Ni, 2.7% Mo)

Figure 1. Autoclave with tubular loop and impeller.



which is similar to stainless 316. It was somewhat corroded from earlier use. The other (B) was made of Sandvik Sanicro 28 (27% Cr, 31% Ni, 3.5% Mo, 1% Cu) and quite new at the beginning of these experiments. When closed, the free volume of A is 1920 ml, B 1890 ml. (Fig. 1)

After each heating period, the autoclave is cooled to room temperature in ice water. The temperature variation as a function of time during heating to 260°C and subsequent cooling is shown in Fig. 2. The content is 1 litre of water. Gas samples are analysed by mass spectrometry, liquid samples by anion chromatography (column Dionex 4000).

1.2. Experimental Details

Oxidative Decomposition

The decomposition of formic acid/formiate performed by the reaction with molecular O_2 is described by the following reactions

$$HCOOH + 1/2\ O_2 \rightarrow CO_2 + H_2O \quad (1)$$
$$HCOO^- + 1/2\ O_2 \rightarrow HCO_3^- \quad (2)$$

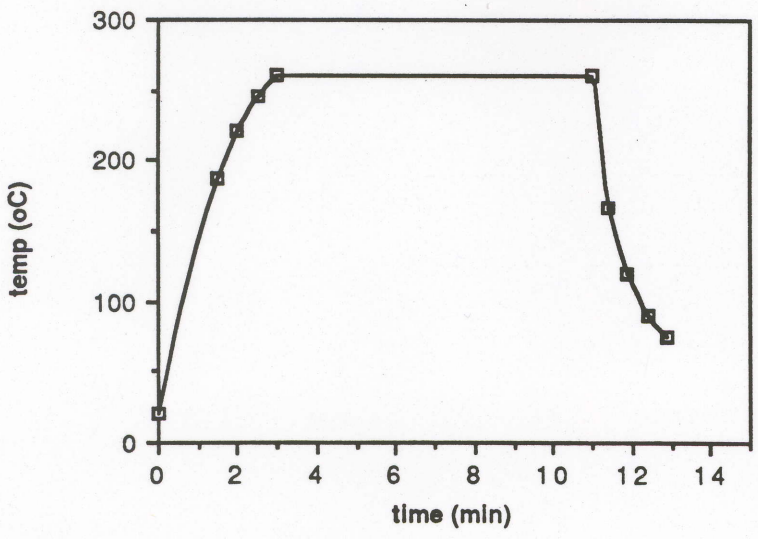
Two experiments were made to compare the formic acid and formiate. Since there were indications that the course of the reaction differed in the two autoclaves another experiment was made with formic acid to examine the catalytic effect of the reactor walls.

Finally, two experiments were carried out to investigate possible influence of other components present, as found by G. Friedhofen et al. (7). Acetic acid and acetaldehyde which frequently occur in practice were chosen for this purpose.

The conditions are given in table 1.

In all experiments a solution in 1 litre H_2O was heated to 260°C. The temperature was kept for 10 minutes, and then cooled to room temperature where gas and liquid samples were taken. If the experiment should be continued, the operation was repeated for yet another period and each time with a new gas charge of 19 bars O_2.

Figure 2. Heating and cooling profile.



Experiment 1

No gaseous component evolved. The pH rose from 7.2 to 8.1 owing to the transformation of formiate to bicarbonate.

The remaining formiate is shown in table 2.

Table 1: Conditions under oxidative decomposition.

Exp.	Autoclave	Bar O_2-press.	Bar atm. press.	Weight of formic acid/ formiate	Other components	Reaction time Minutes
1	A	19	1	6.2 g Na-formiate	–	10, 30, 60
2	A	19	1	6.1 g formic acid	–	10, 20, 30
3	B	19	1	6.1 g formic acid	–	10, 20, 30
4	B	19	1	6.1 g formic acid	6.3 g acetic acid	10, 20, 30
5	B	19	1	4.88 g formic acid	2.35 g acetaldehyde	10, 20, 30

Table 2: Formiate remaining after wet oxidation.

Time at 260°C	0	10	30	60 min
mg/L HCOO-	4200	2800	1540	480 min

Table 3: Gas composition after wet oxidation of formic acid (A).

%	N_2	O_2	Ar	H_2	CO	CO_2	CH_4
10 min	3.8	86.7	0.1	0.82	0.09	8.4	< 0.01
20 min	4.1	92.8	0.1	0.17	0.03	2.8	-
30 min	3.5	95.7	0.09	< 0.01	< 0.005	0.7	-

Table 4: Formic acid remaining after wet oxidation.

Time at 260°C	0	10	20	30 min
mg/L HCOOH	6100	995	43	7

Experiment 2

In this case, a considerable amount of gas is produced as seen from table 3, while the remaining formic acid is shown in table 4.

Mass Balance

Initially, the 0.92 litre gas volume at 20°C equals 0.0383 mol of atmospheric air with 78.3% N_2. Since the nitrogen is untouched by the reaction, it can be calculated from the analysis after 10 min that the autoclave contains 0.788 mol of gas. The percentages of CO_2 and CO then correspond to 0.80g of C. The amount of formic acid converted represents 1.337g of C. The balance 0.537g is made up of CO_2 dissolved in the water, in fine agreement with Henry's law and the solubility at 30°C (the sampling temperature).

If the same procedure is used at 20 min it appears that the formic acid converted corresponds directly to the CO + CO_2 in the gas phase. This is understandable as we remember that the liquid in this case is saturated with CO_2 beforehand. For the same reason, it is not possible to establish the balance after 30 min since the very small quantity of CO_2 formed is i overshadowed by that given off by the liquid.

Experiment 3

Conditions are identical to experiment 2 except that the autoclave is the new one (B). The gas analysis is shown in table 5, while the remaining formic acid is shown in table 6.

Table 5: Gas composition after wet oxidation of formic acid (B).

%	N_2	O_2	Ar	H_2	CO	CO_2
10 min	3.0	92.8	0.19	0.88	0.1	3.0
20 min	5.5	87.8	0.17	0.37	0.1	5.0
30 min	2.8	94.5	0.18	0.48	<0.01	2.0

Table 6: Formic acid remaining after wet oxidation (B)

Time at 260°C	0	10	20	30 min
mg/l HCOOH	6100	4200	870	330

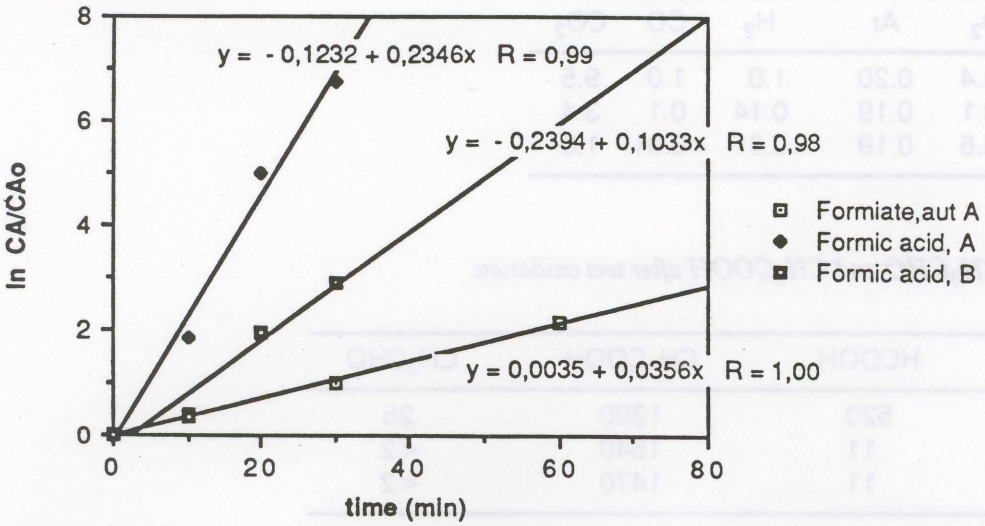


Figure 3. Test of pseudo-first order reaction rate.

At the applied conditions with a large surplus of oxygen, the reactions may be considered pseudo first order. Accordingly, as shown in figure 3, the plot of ln C_A/C_{Ao} versus time consists of straight lines, the slopes of which indicate the reaction rate constants.

Experiment 4

Same conditions as experiment 3 except that 6.3 g of acetic acid are added. The gas analysis is shown in table 7 and the remaining formic and acetic acid in table 8.

Table 7: Gas composition after wet oxidation of formic and acetic acids.

%	N_2	O_2	Ar	H_2	CO	CO_2
10 min	5.4	88.2	0.2	2.0	0.3	3.9
20 min	Sample containers leaky					
30 min						

Table 8: HCOOH and CH_3COOH remaining after wet oxidation.

Time at 260°C	0	10	20	30 min
mg/l HCOOH	6100	3200	150	< 25
CH_3COOH	6300	6275	5800	5600

Table 9: Gas composition after wet oxidation of HCOOH and CH_3CHO.

%	N_2	O_2	Ar	H_2	CO	CO_2
10 min	3.8	84.4	0.20	1.0	1.0	9.5
20 min	3.2	93.1	0.19	0.14	0.1	3.4
30 min	3.2	95.6	0.19	< 0.01	< 0.01	1.0

Table 10: HCOOH, CH_3CHO and CH_3COOH after wet oxidation.

ppm	HCOOH	CH_3COOH	CH_3CHO
10 min	520	1300	25
20 min	11	1540	< 2
30 min	11	1470	< 2

Experiment 5

Wet oxidation of 4.88 g HCOOH + 2.35 g CH_3CHO.
The gas analysis is shown in table 9 and the content of HCOOH, CH_3COOH and CH_3CHO in table 10.

1.3. Non-oxidative Decomposition

Studies on decomposition of formic acid have been focused on gas phase reactions. A model for the decarboxylation of formic acid involves a molecule of H_2O as catalyst for the reaction scheme (3), implying that the H_2 formed takes one H from HCOOH and the other from HOH (8) as illustrated in fig. 4 and the corresponding reaction scheme (eq. 3).

Figure 4. Decarboxylation of formic acid catalyzed by H_2O.

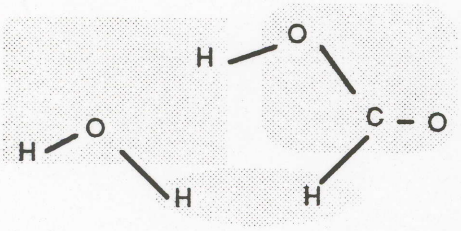


Table 11: Conditions under non-oxidative decomposition.

Exp.	Autoclave	N_2-pressure bar	Atm. pressure bar	Weight of formic acid	Other components
6	A	5.5	0	6.1 g	-
7	B	5.5	0	6.1 g	-
8	B	5.5	0	6.1 g	1 g catalyst

$$HCOOH \xrightarrow{H_2O} CO_2 + H_2 \qquad (3)$$

The formation of H_2 from HCOOH alone is less probable since the activation energy for this reaction (eq. 4) is high.

$$HCOOH \rightarrow CO_2 + H_2 \qquad (4)$$

Also heterogeneous catalysts, for example $Fe_{80}B_{20}$ may highly promote the decarboxylation (5).

Alternatively, formic acid may undergo a dehydration:

$$HCOOH \rightarrow H_2O + CO \qquad (5)$$

The energy level for this reaction lies between the energy levels in reactions eqs. 3 and 4.

Three experiments were carried out investigating the decomposition of formic acid in water with and without a catalyst. The conditions are shown in table 11. Samples were taken as described before.

As it will be seen below, there is a conspicuous difference between the course of experiments 6 and 7. An obvious reason seems to be that the surface of the reactor vessel in (A) is rough and corroded from wear and tear, whereas in (B) it is new. So we tried to etch the wall of (A) with 5% HF by which some of the corroded surface dissolved. The solution was neutralized with NaOH, and the precipitate so formed was dried and added to the content of the autoclave (B) in experiment 8. It amounted to 1 gramme of approx. composition: 75% Fe_2O_3, 12% Cr_2O_3, 10% NiO and small quantities of Cu and Mo.

Experiment 6

The conditions are similar to experiment 2 except that the gas phase is 5.5 bar pure N_2. The reaction produces a considerable amount of gas, the analysis of which is shown in table 12.

Mass Balance

The initial gas volume of the autoclave, 0.92 litre represents 0.21 mol of N_2 at 20°C and 5.5 bar. After the reaction the percentage of N_2 is 48% from which it appears that the gas content now totals 0.438 mol. Since CO_2 originates from the reaction $HCOOH \rightarrow CO_2 + H_2$, it is permissible to measure CO_2 by the volume of H_2 which is slightly dissolved in H_2O. The calculated amount of C

Table 12: Gas composition after 30 min decomposition of formic acid in autoclave A.

%	N_2	O_2	Ar	H_2	CO	CO_2
	48	0.04	<0.002	30.7	0.4	20.2

Formic acid left in the liquid 33 mg/l.

Table 13: Gas composition after decomposition of formic acid in autoclave B.

%	N_2	O_2	Ar	H_2	CO	CO_2
	80.7	0.24	0.01	9.6	3.5	6.0

Formic acid left 4800 mg/l

in CO_2 + CO is then 1.635 g while the decomposed HCOOH represents 1.583 g of carbon.

Experiment 7

Same conditions as in experiment 6 except that autoclave B is used. Much less gas is produced as seen from table 13.

Mass Balance

The initial gas volume, 0.89 litre, represents 0.20 mol of N_2 at 20°C and 5.5 bar. After the reaction there is 80.7% of N_2 corresponding to a total of 0.24 mol. As in experiment 6 we take H_2 to be a measure of the total amount of CO_2. Together with CO it gives us 0.393g of carbon in the gas produced while the 1.3g of formic acid converted corresponds to 0.339g C.

Experiment 8

Conditions are the same as in experiment 7, but with the addition of corrosion products from autoclave (A). More formic acid is converted than in experiment 7 as seen from table 14.

Mass Balance

The initial amount of N_2 is 0.20 mol. After the reaction there is 61.3% N_2, corresponding to a total of 0.326 mol.

Total carbon in gas 1.04g C. 3.7g formic acid converted ~ 0.965 g C.

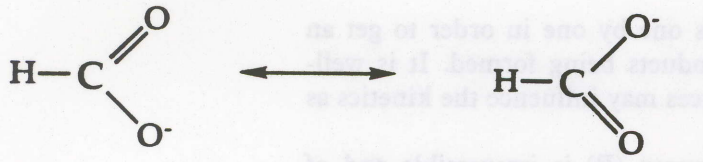
Table 14: Gas composition after anaerobic decomposition of formic acid in autoclave B with catalyst.

%	N_2	O_2	Ar	H_2	CO	CO_2
	61.3	0.06	0.01	25.8	0.8	12.0

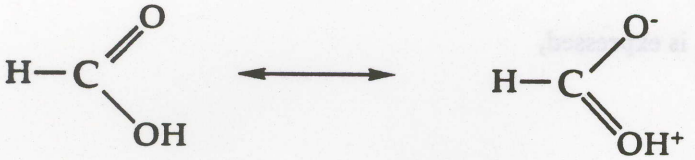
Formic acid left 2400 mg/L.

1.4. Discussion

We see immediately that the oxidation of formiate is six times slower than that of formic acid. The ion $HCOO^-$ is most likely stabilized by resonance between the two identical structures



whereas in the corresponding case for the acid



the second form is only of slight importance.

Further, the occurrence of H_2 in the reaction products indicates that a decarboxylation takes place along with the oxidation. The difference in reaction rates between experiments 2 and 3 must be due to a catalytic effect of the wall of the reaction vessel. Adding acetic acid seems to accelerate the decomposition of formic acid, also by way of decarboxylation as evidenced by a higher H_2 content in the reaction products.

With acetaldehyde added, the decomposition of formic acid is even more rapid. To some extent it may be caused by the acetic acid produced by the oxidation of acetaldehyde.

It is seen that the non-oxidative decomposition of formic acid follows mainly the decarboxylation route. The catalyzed process seems to be exclusively a decarboxylation. By adding the corrosion products from autoclave A to B, we have made it likely that these are responsible for the catalytic effect. The oxidative decomposition is also catalysed, but to a lesser extent.

Comparing experiments 3 and 7, both in autoclave B, the oxidation is seen to result in a faster removal of formic acid. On the other hand, the reaction rates in experiments 2 and 6 must be comparable judging from the formic acid left. Since there is very little H_2 in the reaction products after oxidative decomposition and H_2 is not oxidized, it can be deducted that the hydrogen produced by the decarboxylation is in a reactive state which is rapidly oxidized.

1.5. Conclusions

In aqueous solutions of formic acid at an elevated temperature, both oxidative and non-oxidative decompositions occur. Mixed oxides of stainless steel components catalyse both reactions, in particular the decarboxylation of HCOOH.

The formiate ion is also oxidized, but more slowly, to bicarbonate.

2. Wet Oxidation of Low Molecular Carboxyl Acids

Wet oxidation of acetic acid is investigated along with propionic acid, butyric acid, isobutyric acid (the first branched-off acid in the line), and α-hydroxy isobutyric acid.

It is our initial aim to consider the acids one by one in order to get an impression of the reaction rate and the products being formed. It is well-known that the presence of different substances may influence the kinetics as well as the mechanisms (7).

The reaction of formic acid (A) with oxygen (B) is irreversible and of second order:

$$A + B \rightarrow \text{Product}$$

With the concentration C, the reaction rate r_A is expressed,

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k\,C_A C_B$$

If one component, e.g. O_2, is in large surplus, C_B can be considered constant, so that the reaction rate is,

$$-r_A = -\frac{dC_A}{dt} = k'C_A$$

The reaction is now of pseudo first order. By integration

$$-\ln\frac{C_A}{C_{Ao}} = k't$$

Where k' is the rate constant, and C_A the initial concentration for the reactant A.

According to the literature, acetic acid is converted only slowly or not at all, while propionic acid is oxidized in two different ways (10):

1) directly to CO_2
2) to acetic acid via acetaldehyde

Similarly, the butyric acid is transformed to acetic acid via acetaldehyde (9).

As minor quantities of propionic acid and formic acid are produced during the reaction, the following mechanisms are proposed (10):

$$\overset{\beta\quad\alpha}{CH_3CH_2CH_2COOH} \rightarrow CH_3CH_2COOH + HCOOH$$

$$\overset{?\quad O_2\quad ?}{}$$

Formic acid is further oxidized to CO_2 while propionic acid is attacked by oxygen at the α-carbon atom, analogous to the above-mentioned example. However, it has been stated that the α-carbon atom is in a deactivated state, so that β-carbon is the point of attack instead. Under the section results and discussion, a proposal of a reaction mechanism is suggested.

Regardless of the reaction mechanism, these reactions are reduced to pseudo first order, as shown above, provided the oxygen concentration can be considered constant during the experiment.

More complex molecules such as phenol and chlorophenol are alleged to end up as formic acid and acetaldehyde (1). However, it is shown here how these reducing substances will not resist an oxidation.

Up to now, no information has been found in the literature on wet oxidation of formic acid, acetaldehyde, isobutyric acid, and higher fatty acids. However, the thermal stability of formic acid has been studied. It is shown that H_2O catalyzes the decarboxylation of formic acid to CO_2 and H_2 at 500°C (8).

2.1. Methods and Materials

All experiments take place in a loop autoclave, described on page 3.

In all experiments, analytical-grade chemicals and demineralised water were used. The initial concentrations are 0.1 molar, if nothing else is stated. 19 bar O_2 is added to the atmospheric air in the autoclave. Samples of liquids and gases are taken at predetermined times, after cooling the autoclave to 35°C. Gas samples are taken thorugh a valve, whereas the liquid sampling requires that the autoclave be opened. After sealing the autoclave, the same procedure as before is applied and the experiment continues for the desired time.

The organic acids are determined on a Dionex ion chromatograph 4000 i, column HPICE ASI, flow 0.8 ml/min. Eluent 1mM HCL suprapur regenerant, and 5 mM tetrabutyl ammonium hydroxide. The organic acids are diluted by 1mM HCL.

2.2. Results and Discussion

Rate constants

The experimental details are explained in table 15.
In Figs. 5 and 6 the calculation of the rate constants ensues from the first-order reaction test.

The rate constant for formic acid appears from table 16 to be several orders of magnitude above the other acids. Apart from the formic acid, there is a tendency for the decomposability to rise with the number of carbon atoms. Branching in the molecule also yields a greater decomposability. If an α-hydroxy group is introduced the reaction rate rises very sharply (k' = 0.0067 for isobutyric acid, and k' = 0.1036 for α-hydroxy isobutyric acid).

Table 15: Experimental details.

Experiment	Component	Weight/g	Time/min
1	formiate	6,4	10,30,60
2	formic acid	6,1	10,20,30
3	acetic acid	6,5	30,60,90
4	propiopic acid	7,7	30,60,90
5	butyric acid	8,7	30,60,90
6	isobutyric acid	7,45	30,60,90
7	α-OH-isobutyric acid	9,0	30,60,90

Table 16: Rate constants.

Component	k'/min^{-1}
formic acid	0.2346
formiate ion	0.0356
acetic acid	0.0010
propionic acid	0.0022
butyric acid	0.0046
isobutyric acid	0.0067
α-H-isobutyric acid	0.1036

Wet oxidation of lower aliphatic carboxyl acids is thus characterized by pseudo first-order kinetics, and as it will appear from the following, by formation of organic products with a relatively poor yield.

Products of decomposition and reaction mechanisms

As mentioned above, acetic acid is slowly decomposed, and the products are CO_2 and formic acid.

Propionic acid is transformed to CO_2, formic acid, and acetic acid; the course is indicated in Fig. 7. Butyric acid is transformed to CO_2, formic acid, acetic acid, and propionic acid (see Fig. 8). Both the isobutyric acid and α-OH-isobutyric acid are transformed to CO_2, formic acid, and acetic acid, but the yields are very different, as is seen in Figures 9 and 10.

The concentrations of the products of transformation increase during oxidation of propionic acid and buturic acid. With isobutyric acid, which is more easily oxidized, the acetic acid concentration reaches a higher level. The same is true for the formic acid concentrations, but after 30 min. the concentration falls because formic acid is consumed by further decomposition. During oxidation of α-OH-isobutyric acid, the tendency is even more distinct, as the acetic acid concentration also falls slightly after a reaction time of 60 min. In this case, the concentration of formic acid is comparable to that of α-OH-isobutyric acid, which finally vanishes. The concentration of acetic acid, on the contrary, reaches a value corresponding to the initial concentration of α-OH-isobutyric acid (see Fig. 10).

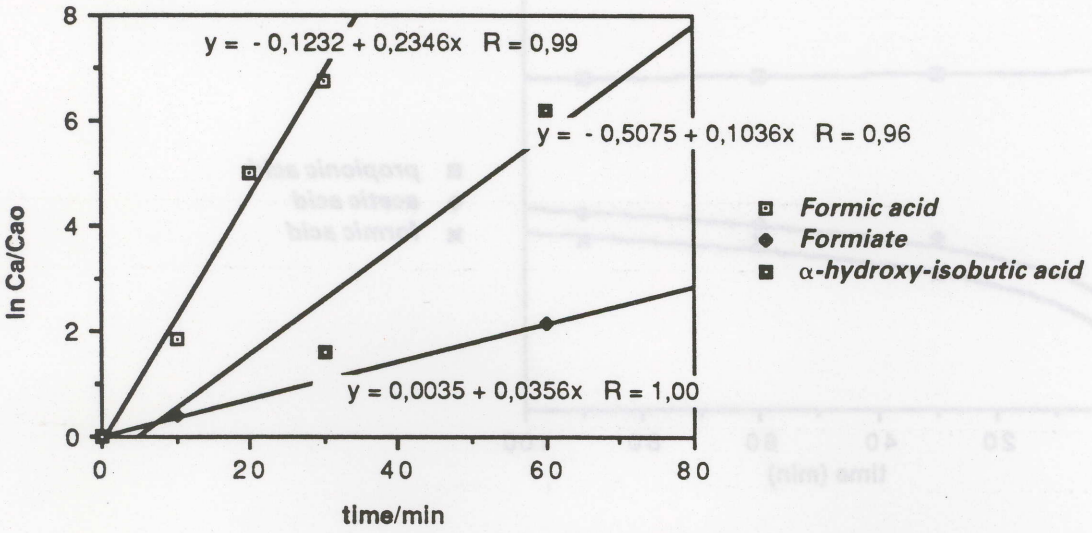
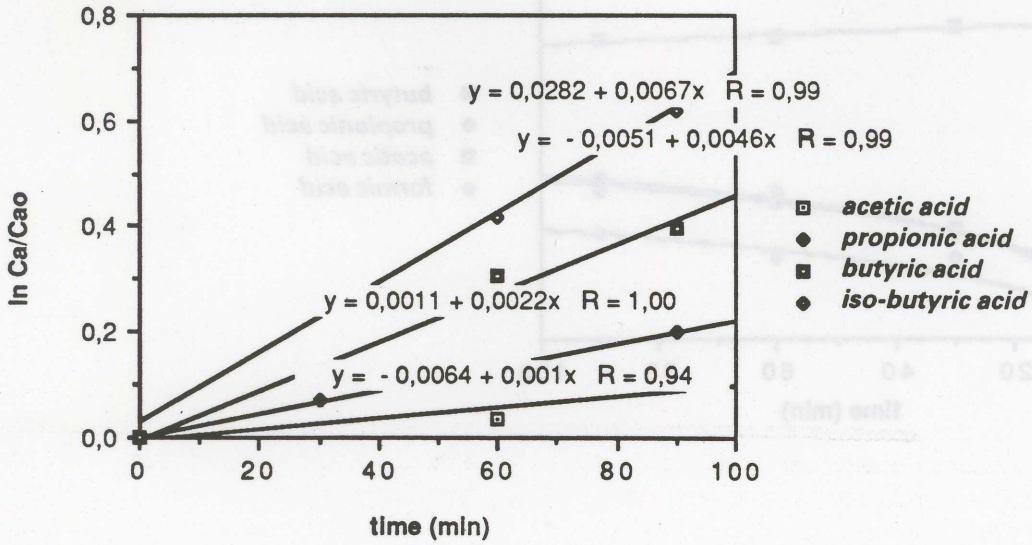


Figure 5. Calculation of the rate constants for formic acid, formiate, and α-hydroxy isobutyric acid.

Figure 6: Calculation of the rate constants for acetic acid, propionic acid, butyric acid, and isobutyric acid.



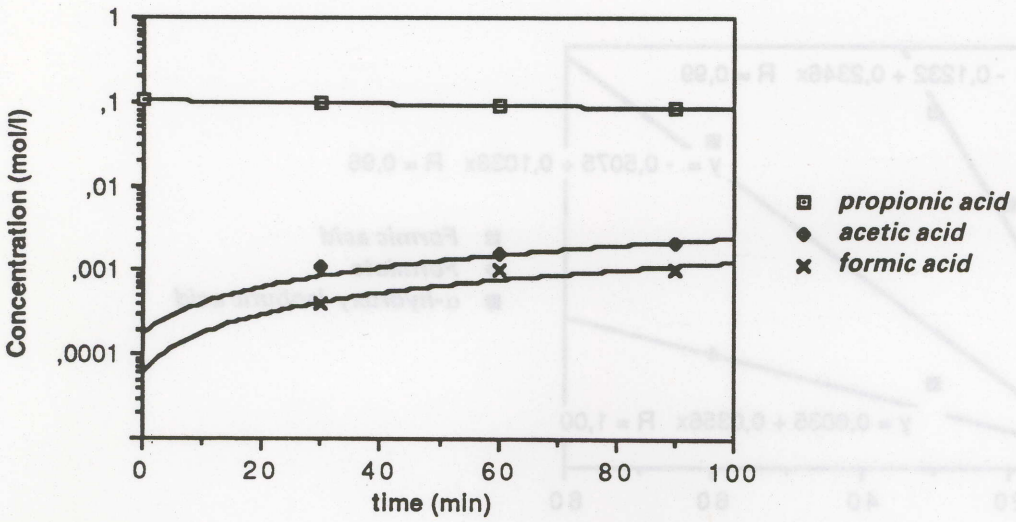
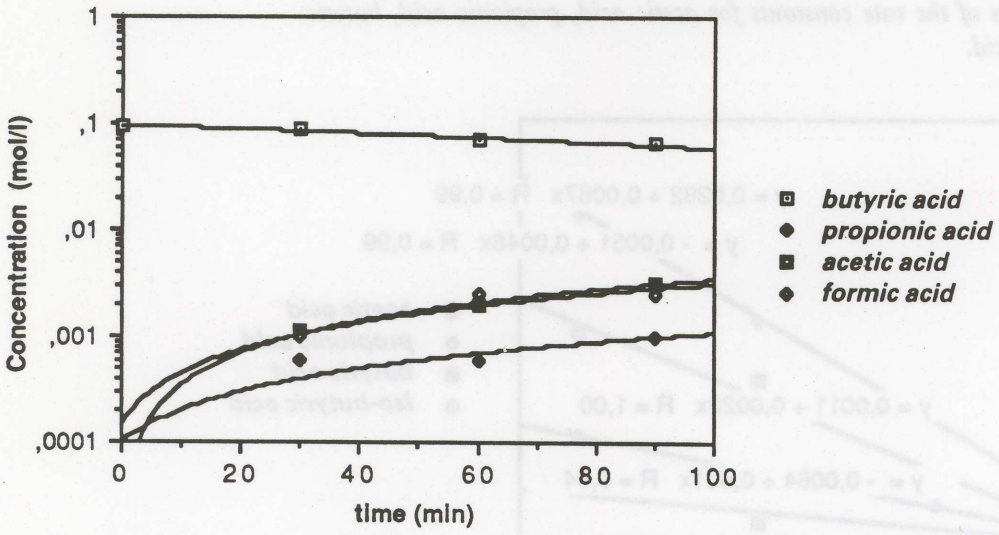


Figure 7: Decomposition of propionic acid and its products of transformation.

Figure 8. Decomposition of butyric acid and its products of transformation.



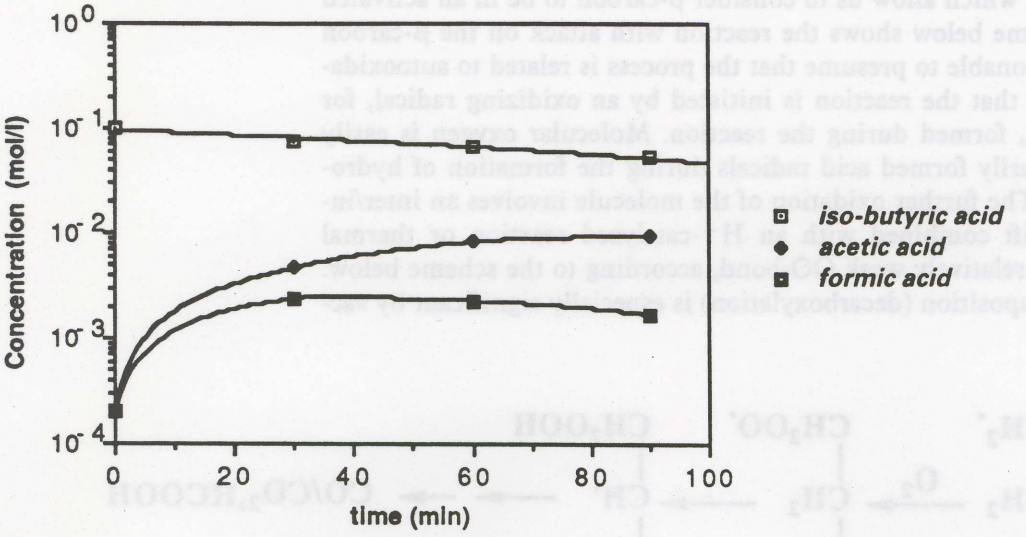
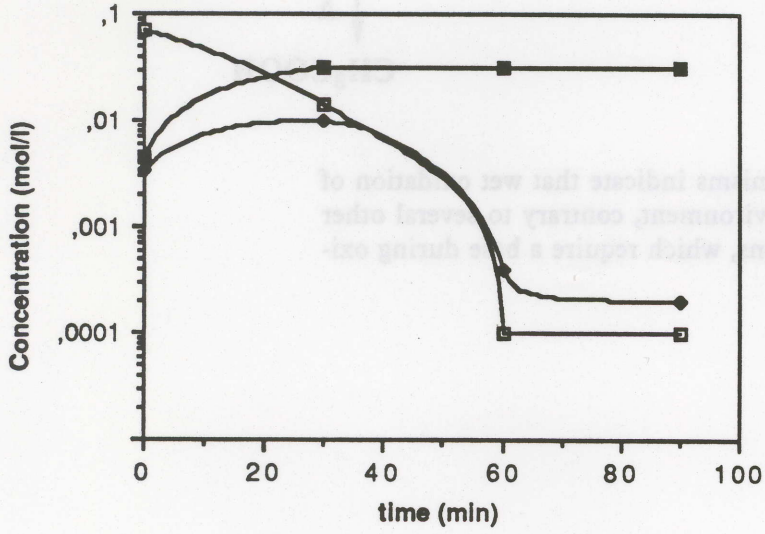
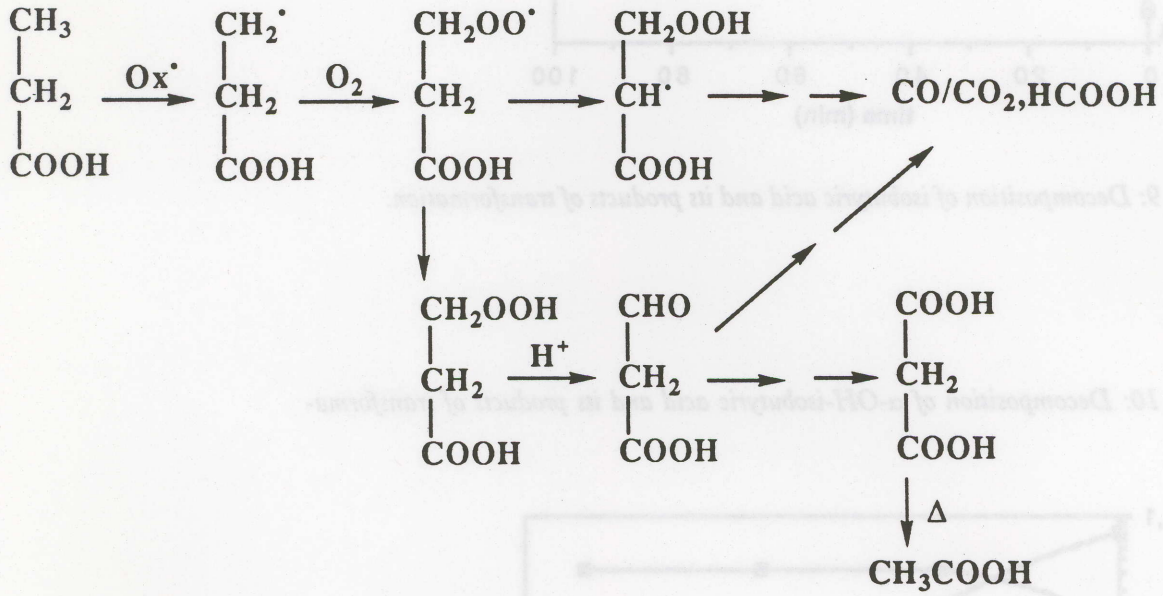


Figure 9: Decomposition of isobutyric acid and its products of transformation.

Figure 10: Decomposition of α-OH-isobutyric acid and its products of transformation.



The rate constants found indicate that the attack point is not the α-carbon atom, but a more remote one, as the reaction rate increases with the number of carbon atoms. Note that the high stability of CH_3COOH reflects a deactivated α-carbon atom, which allow us to consider β-carbon to be in an activated position. The scheme below shows the reaction with attack on the β-carbon atom. It seems reasonable to presume that the process is related to autooxidation, which means that the reaction is initiated by an oxidizing radical, for example $HO_2\cdot/\cdot OH$, formed during the reaction. Molecular oxygen is easily added to the primarily formed acid radicals during the formation of hydroperoxide radicals. The further oxidation of the molecule involves an inter/intramolecular H-shift combined with an H^+-catalyzed reaction or thermal dissociation of the relatively weak OO-bond, according to the scheme below. The thermal decomposition (decarboxylation) is especially significant by »activated« acids.



The above-mentioned reaction mechanisms indicate that wet oxidation of organic acids is promoted in an acid environment, contrary to several other organic pollutants including hydrocarbons, which require a base during oxidation.

2.3. References

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Thermal and Oxidative Decomposition of Lower Fatty Acid with Special Attention to Formic Acid

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Abstract. Low molecular carboxyl acids are important intermediate products of wet combustion of organic pollutants. This article deals with the reaction rates and mecanisms of some of these acids under wet oxidation conditions. It appears from the investigations that the rate of decomposition increases by the number of carbon atoms as larger molecules decompose into smaller ones and CO_2. An exception is formic acid, the lower end member of the fatty acid series, which decomposes by both oxidative and non- oxidative routes at a rate several times higher than that of the other compounds tried.

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